APPLICATION OF SWELLING TECHNIQUES TO PROPELLANTS AND BINDERS

by

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INTRODUCTION

The use of elastomers in solid rocket powerplants was recently discussed by Sayles [1]. A controlled rate of energy release from a solid rocket motor depends upon the maintenance of its structural integrity until burnout. The propellant grain must serve as a structural member of the system and withstand thermal, acceleration, and pressurization loadings. An uncontrolled increase in the surface available to the flame front often results in catastrophic failure. Therefore, propellants must be evaluated throughout their whole life span to establish their current suitability for a designated application.

The propellants under discussion consist of lightly crosslinked rubbery binders filled with up to 70% by volume of crystalline inorganic and metallic particles. The relationships between their bulk properties and their physical and chemical properties are greatly affected by interactions between the binders and fillers. This paper gives examples of the use of the Bills and Salcedo [2] technique which involves swelling the filled samples in an appropriate solvent to overcome these interaction effects in order to elucidate

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the chemistry of several types of propellant binders. Results are reported on one polyurethane and two carboxyl-terminated polybutadiene (CTPB) gumstocks, several CTPB propellants, a polyurethane and a polysulfide propellant.

EXPERIMENTAL

Materials - The following materials were tested:

(1) Binder I - CTPB crosslinked with curing agent 1 and curing agent 3.

(2) Binder II - CTPB crosslinked with curing agent 1, curing agent 2, and curing agent 3.

(3) Binder III - A polyurethane consisting of an aliphatic diisocyanate, a polyether glycol chain extender, a tetrafunctional polyester glycol and a triol crosslinking agent.

(4) Propellant I - Same composition as Binder I with aluminum and ammonium perchlorate.

(5) Propellant II - Same composition as Binder II with aluminum and ammonium perchlorate.

(6) Propellant III - Same composition as Binder III with aluminum and ammonium perchlorate.

(7) Propellant IV - CTPB crosslinked with curing agent 1 and curing agent 2.

(8) Propellants V & VI - CTPB crosslinked with curing agent 1 and curing agent 4.

(9) Propellant VII - Polysulfide.

Procedures - Two swelling procedures were used. In the first procedure, a sol-gel ratio determination, the samples were extracted with methylene chloride in a Soxhlet extractor equipped with a drying tube for a period of about 96 hours. The swollen and dried extracted samples were weighed. The sol weights were obtained by evaporation of the solvent.

The densities of the samples were measured in a Fisher air-comparison pycnometer; the densities of the extracts were determined by weighing portions of the extracts in previously calibrated micropipettes (0.1 ml).

The sol fraction of propellant binders is usually high, ranging from 30% to 50%. Bills and Salcedo introduced a correction for the high sol fraction in Equations 1 and 2 for calculations of the swelling ratios, Q, and for volume fractions of gel, v_r, respectively.

$$Q = 1/v_2 = \frac{V_S - V_E + \frac{\text{Swollen Wt} - \text{Wt extd sample}}{\text{d solvent}}}{V_S - V_E/v_b} \quad (1)$$

where v_2 is the volume fraction of rubber in the swollen sample, V_S is the volume of sample, V_E is the volume of extract, d is density, and v_b is the volume fraction of binder in the sample [2,3].

$$v_r = \frac{v_b V_S - V_E}{v_b V_S} \quad \text{or} \quad 1 - \frac{V_E}{v_b V_S} \quad (2)$$

In the second swelling procedure, often combined with a compression modulus test, cylinders of the binder of propellant (1 cm high and 1 cm in diameter) were covered with solvent in small beakers. With the carboxyl-terminated polybutadiene propellants, it was necessary to store the swelling samples in a desiccator under an atmosphere of nitrogen over anhydrous calcium sulfate. The solvent was replaced with fresh solvent once or twice during the swelling to remove the sol fraction.

All the solubility parameters were determined by the second swelling procedure.

The crosslink densities were determined by the swollen compression technique of Cluff, Gladding, and Pariser[4]. The numbers of effective chains per unit volume in the binders, ν_e were calculated by Equation 3.

$$\frac{\nu_e}{3\pi} = \frac{h_o S g}{r^2 k T (v_r)^{2/3}} \quad (3)$$

where h_o is the height of the unswollen sample, r the radius of the unswollen sample, S the slope of the line (Δwt/Δ height), g is the gravitational constant, k is the Boltzmann constant, T is the absolute temperature and v_r is the volume fraction of gel in the binder.

RESULTS AND DISCUSSION

Characterization Studies

The swelling ratios of Binders I, II, and III and Propellants II, III, and IV were measured. The solubility

parameters were determined by the procedure of Gee[5]. The plots of $(1/V_o \ln Q_{max} Q^{-1})^{1/2}$ vs $(Eo/Vo)^{1/2}$ for these materials are presented in Figures 1 through 6. Here V_o is the molar volume of the solvent, Q_{max} is the maximum swelling ratio found for the solvents tested, Q is the swelling ratio in the solvent being tested, and $(E_o/V_o)^{1/2}$ is the square root of the cohesive energy density of the solvent, i.e., the solubility parameter of the solvent. E_o is the molar heat of vaporization of the solvent. Most of the values used for V_o and $(E_o/V_o)^{1/2}$ have been those of Bristow and Watson[6]. Results are listed in Table I.

Swelling measurements were part of a recent program designed to determine the conditions required to manufacture a polysulfide propellant on a pilot-plant scale. It was found that the samples which met the specifications for elongation were more highly crosslinked with a higher value for v_r. The values for swelling ratio in methylene chloride, v_r, and maximum elongation, Em are given in Table II. Therefore, a swelling test will be considered as a quality control technique.

The presence of water during the swelling period has a great influence on the results of swelling measurements for propellants. For example, two sets of samples from the same propellant were swollen in dichloroethane. One sample was stored in the presence of a desiccant and the swelling ratio was 3.17 $\pm$ 0.03. The other sample was exposed to

moist air and the swelling ratio was 4.65 ± 0.16.

The compression modulus test is a very convenient method for determining the number of effective chains in an elastomer ν_e, since a separate determination of the solvent-polymer interaction parameter is eliminated. Results of ν_e determinations by the compression of unfilled binder samples swollen in any good solvent for the binder give values that are comparable (Table III). This has been found true for rubber and other elastomers. However, this insensitivity of the crosslink density values to the equivalency of the corresponding solubility parameters does not hold for the solvent swelling of highly filled materials. This disparity may be related to the degree of swelling necessary for C_2 to fall in zero in the Mooney-Rivlin[8] relationships. The change in the calculated number of effective chains is drastic when a poor solvent is used (Figure 7).

Accelerated Aging Studies

The effects of accelerated aging have been followed qualitatively by using the first swelling procedure to differentiate chemical changes occurring in the binder from changes in the physical forces acting between the fillers and binder. This procedure is also useful when the amount of sample is insufficient or the form of the sample is unsuitable for standard mechanical properties testing.

The separation of the chemical affects occurring in the binder from physical interaction between the filler and binder is illustrated by comparison of propellants IV and V. Samples were stored at 160°, 205°, and 240°F for three weeks with weekly withdrawals. The maximum stress, elongation at maximum stress, stress at rupture, elongation at rupture, and Young's modulus were determined at three strain rates at a test temperature of 77°F.

The mechanical properties test showed that propellant IV hardened as a result of the accelerated aging. The results of the swelling tests (Figure 8) are consistent with continued crosslinking of the binder.

The mechanical properties test of propellant V indicated a softening at 160°F. At 205°F an initial softening was followed by embrittlement. At 240°F the material hardened with the major change occurring in the early stages of the storage program. Again the results of the swelling measurements (Figure 9) are consistent with an initial decrease in crosslink density followed by an increase in crosslinking of the binder. These results indicate that ammonium perchlorate and aluminum are nonreinforcing fillers with these binders.

One example where swelling techniques have been of value when physical properties tests could not be run was in a study of the changes in the bonding of a propellant to

a motor insulator during storage. The propellant seemed to be softening but the usual physical properties tests could not be carried out because of the physical makeup of the samples. During the sol-gel determination the propellant samples dissolved, indicating a severe degradation of the gel network.

Recently we have carried out accelerated aging tests on small samples of Propellant I. Less than 50 grams of each of the three different propellant lots were available for storage tests. We studied the changes in $\underline{v_r}$ and $\underline{1/v_2}$ during the 35 days storage period and the changes found for $\underline{v_r}$ are given in Figure 10. An increase in modulus and a decrease in elongation would have been predicted for this propellant.

In another program several gallon-size samples of propellant III which had been stored for over three years at 122°F with little indication of degradation, were found to be flowing out of their containers. Standard mechanical properties specimens could not be prepared because of the presence of the semi-liquid material. Further examination showed the degraded material extended only about one inch from all surfaces of the container. Samples were cut from the unaffected portion of the propellant for swelling measurements. Results confirmed that the bulk of the propellant had not degraded. Checking back on the storage records, it was found that about a month before, the samples had been

exposed to temperatures as high as 150°F for a time, but this misadventure had not been reported. Therefore, the changes in the propellant were due to the accidental changes in its environment and not to a sudden onset of degradative reactions in the propellant.

A quantitative study was made of the effect of humidity during elevated temperature storage of propellant III by the compression modulus method. Dioxane was selected as the swelling solvent (Figure VI). Results (Table IV) showed a slight increase in the number of effective chains with time when the humidity was 25% and a decrease at the 80% humidity level.

SUMMARY

The utility of swelling tests in studies of highly-filled solid propellants and their corresponding binders has been shown. The solubility parameters for two propellants have been shown to be the same as those of the corresponding binders.

The use of swelling measurements as a quality control technique for solid propellants is indicated.

The proper selection of the solvent is critical for crosslink density determinations with a highly filled elastomer. The chemical changes occurring in propellant-binders during high-temperature aging programs may be qualitatively explained by swelling tests and quantitatively determined by the determination of the compression modulus of swollen

samples.

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TABLE I

Values of Solubility Parameter

Designation	Binder	Propellant
I	8.9	---
II	9.25	9.24
III	9.7	9.7
IV	--	9.2

TABLE II

Properties of Polysulfide Propellant

	$1/v_2$	v_r	Em(%)
Unsatisfactory samples	9.10-9.55	.814-.827	6.24-9.74
Satisfactory samples	7.79	.869	14.66

TABLE III

Values of ν_e for Gumstocks

Binder	Swelling Solvent	ν_e (a)	ν_e (b)
Polyurethane	Dioxane	1.65×10^{19}	1.62×10^{19}
Polyurethane	Cyclohexanone	1.75	
Carboxyl-terminated polybutadiene	Xylene	1.37×10^{19}	2.05×10^{19}
"	Benzene	1.24	
"	Chloroform	1.34	
"	Tetrahydro-furan	1.35	

(a) From compression modulus of swollen samples

(b) By extension of unswollen sample

TABLE IV

Effect of Humidity on ν_e for Polyurethane Propellant Stored at 160°F

Time of storage (hr)	Relative humidity	ν_e
Control	--	$1.46 \pm .05 \times 10^{19}$
43	25	1.51
91	25	1.59
168	25	1.59
Control	--	$1.54 \pm .08 \times 10^{19}$
43	80	1.20
143	80	1.25
165	80	1.14

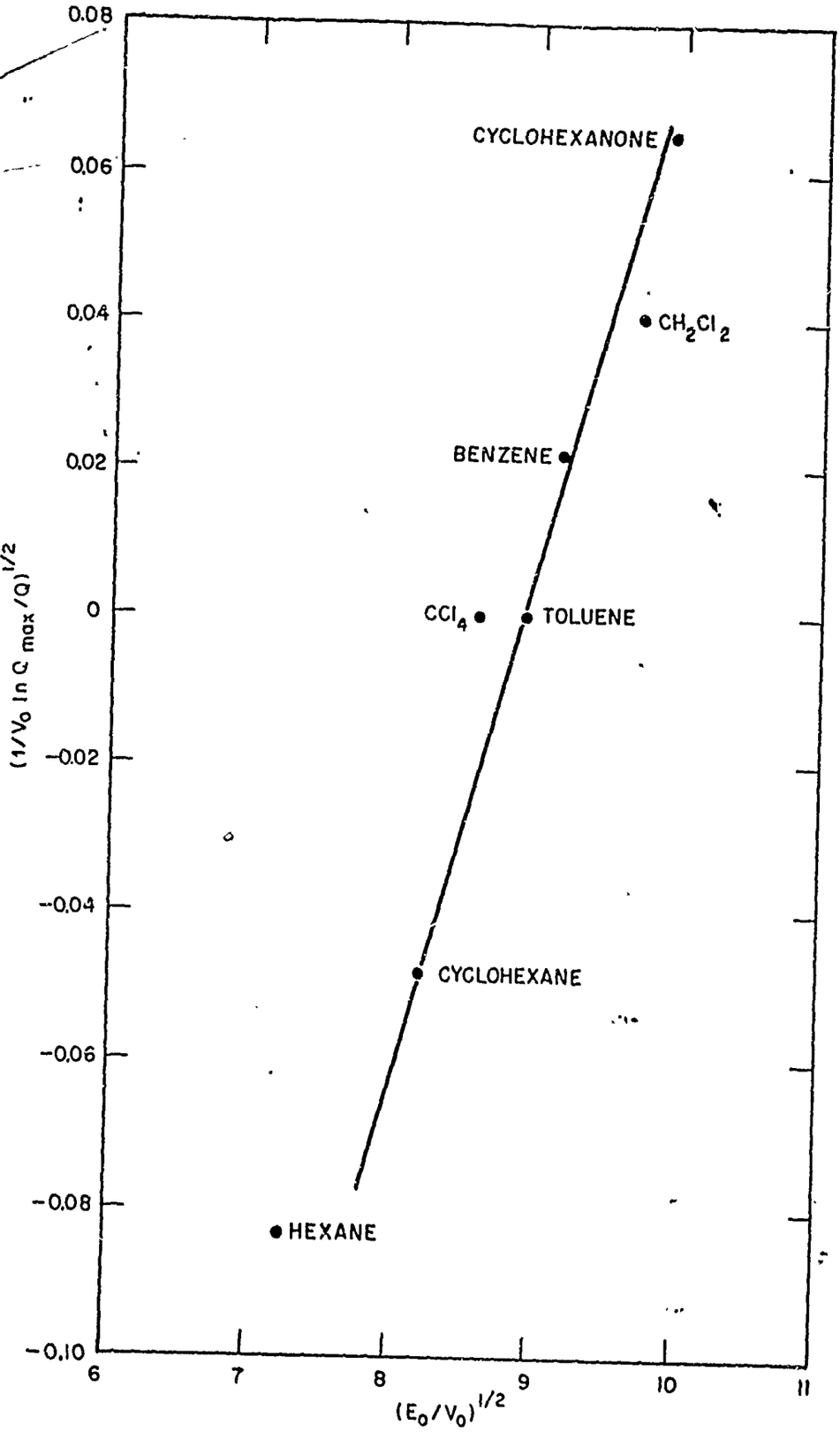

Figure 1—Determination of Solubility Parameter for CTPB Binder I

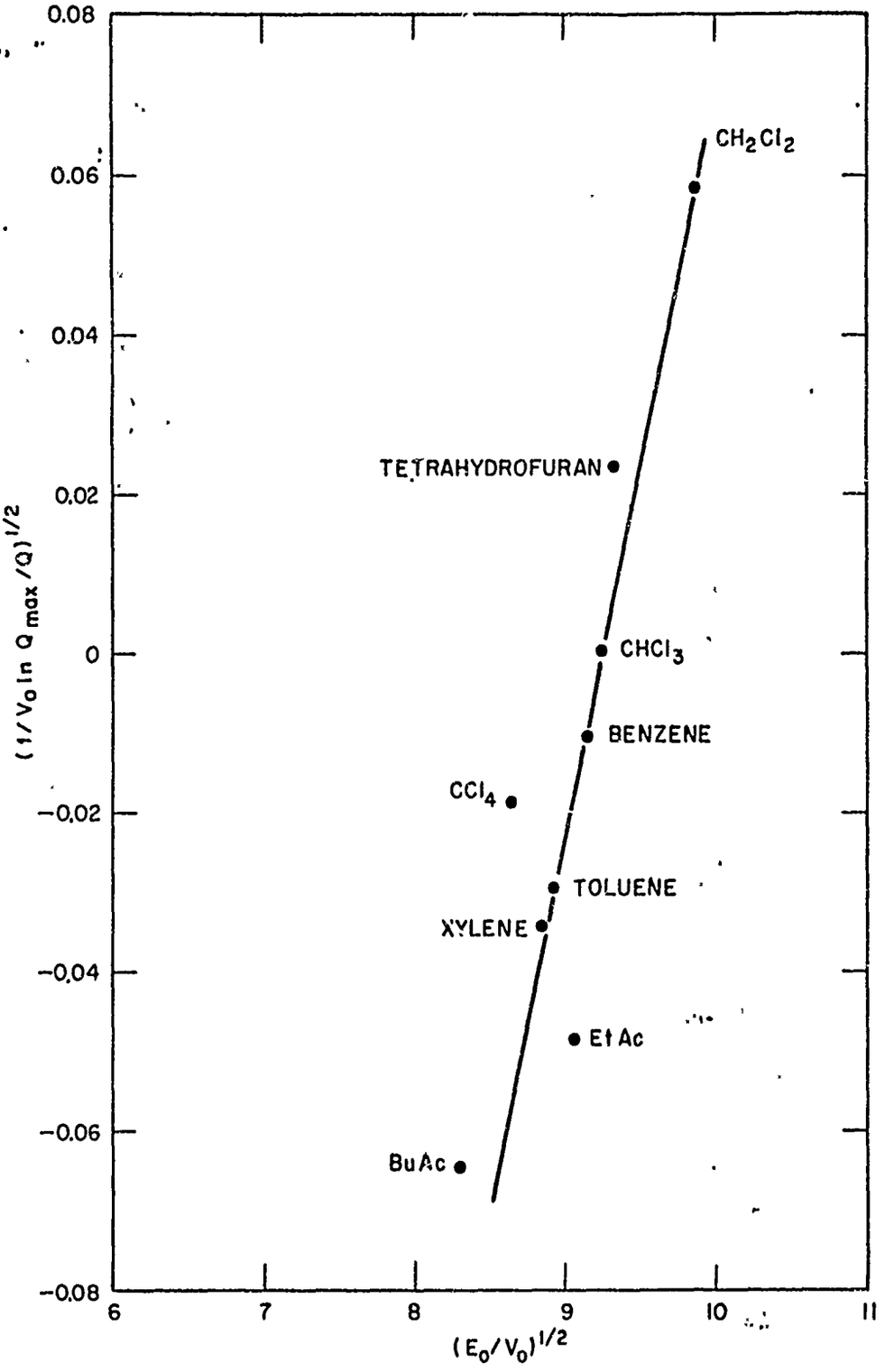

Figure 2— Determination of Solubility Parameter for CTPB Binder II

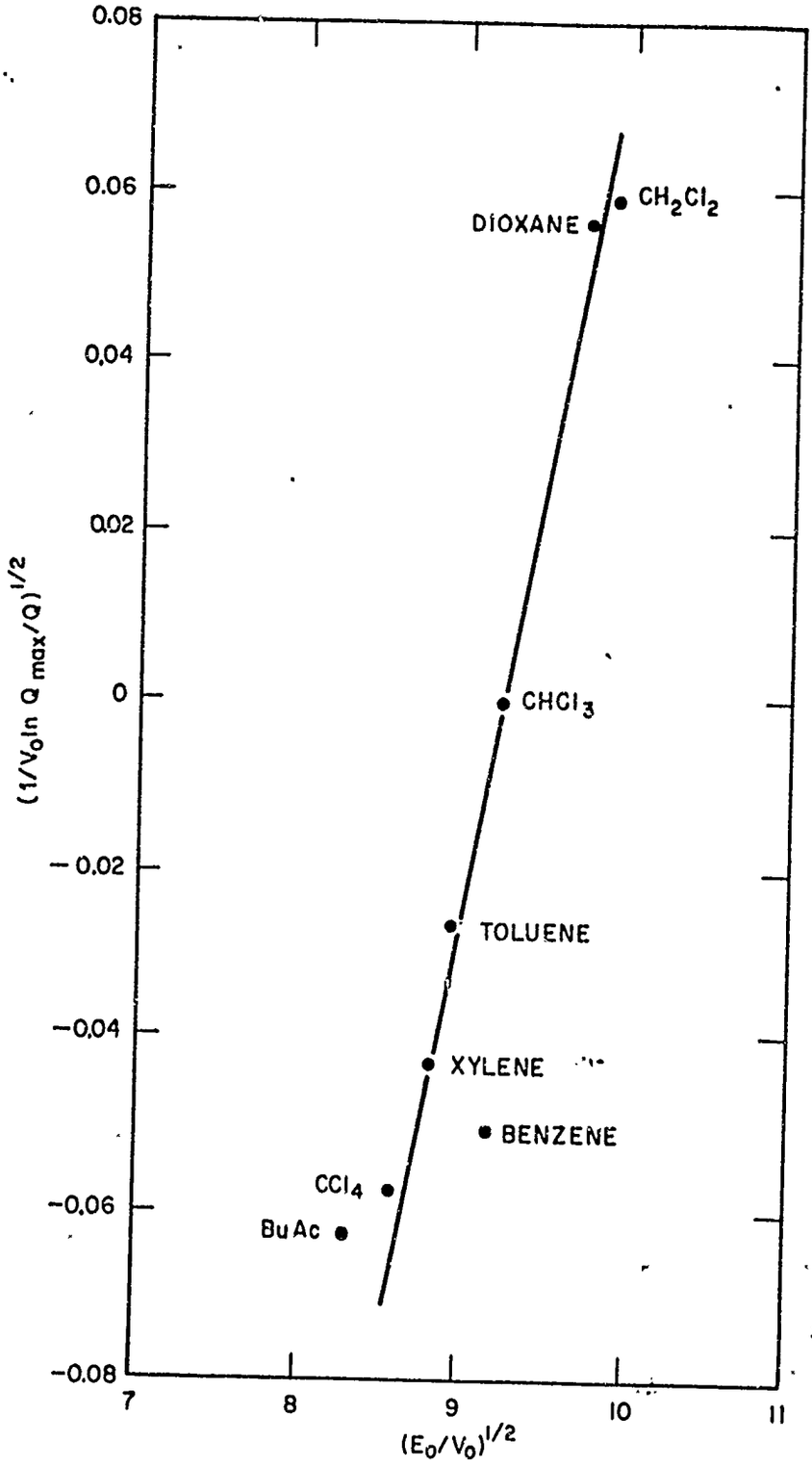

Figure 3– Determination of Solubility Parameter for CTPB Propellant II

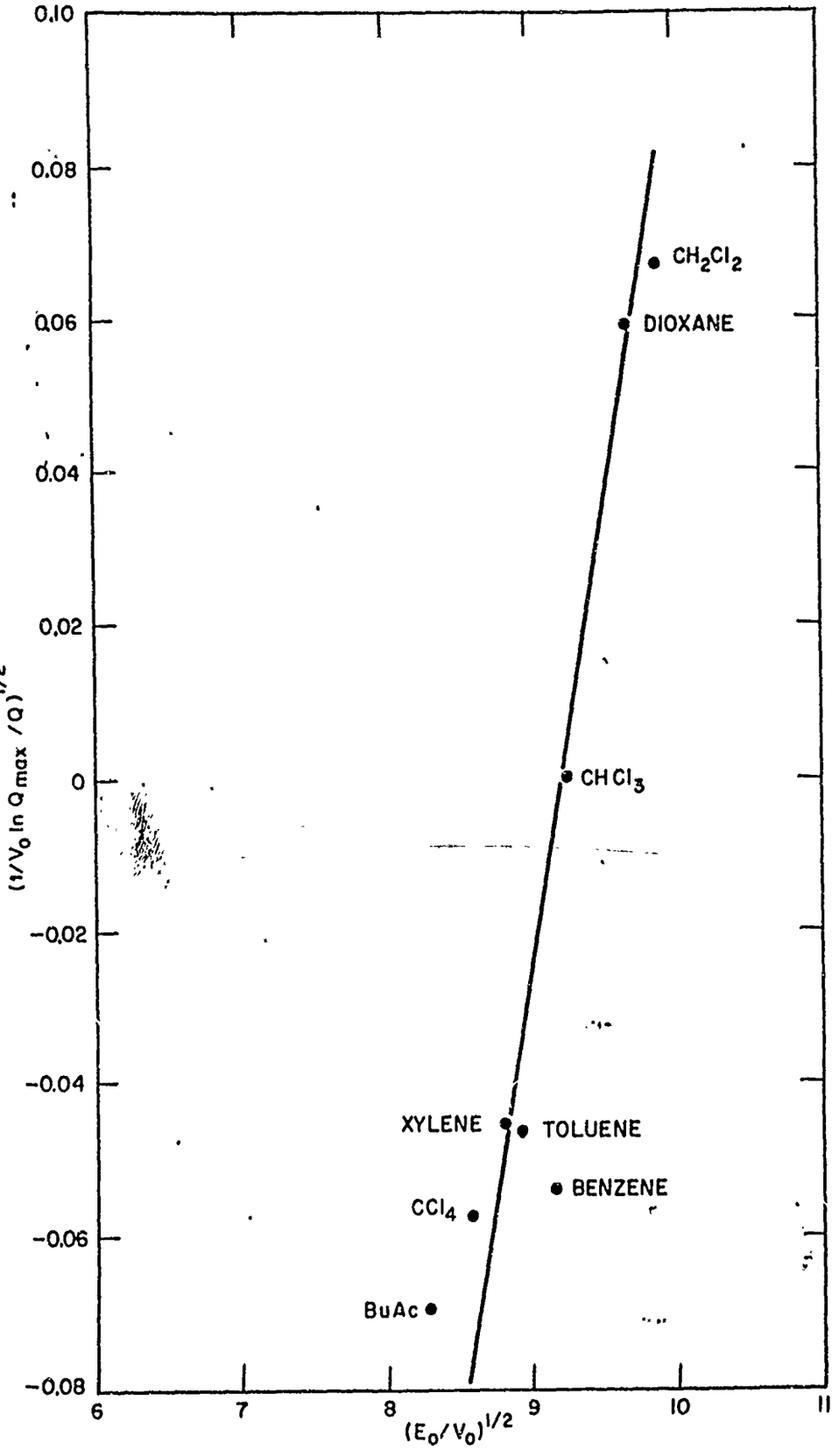

Figure 4 - Determination of Solubility Parameter for CTPB Propellant IX

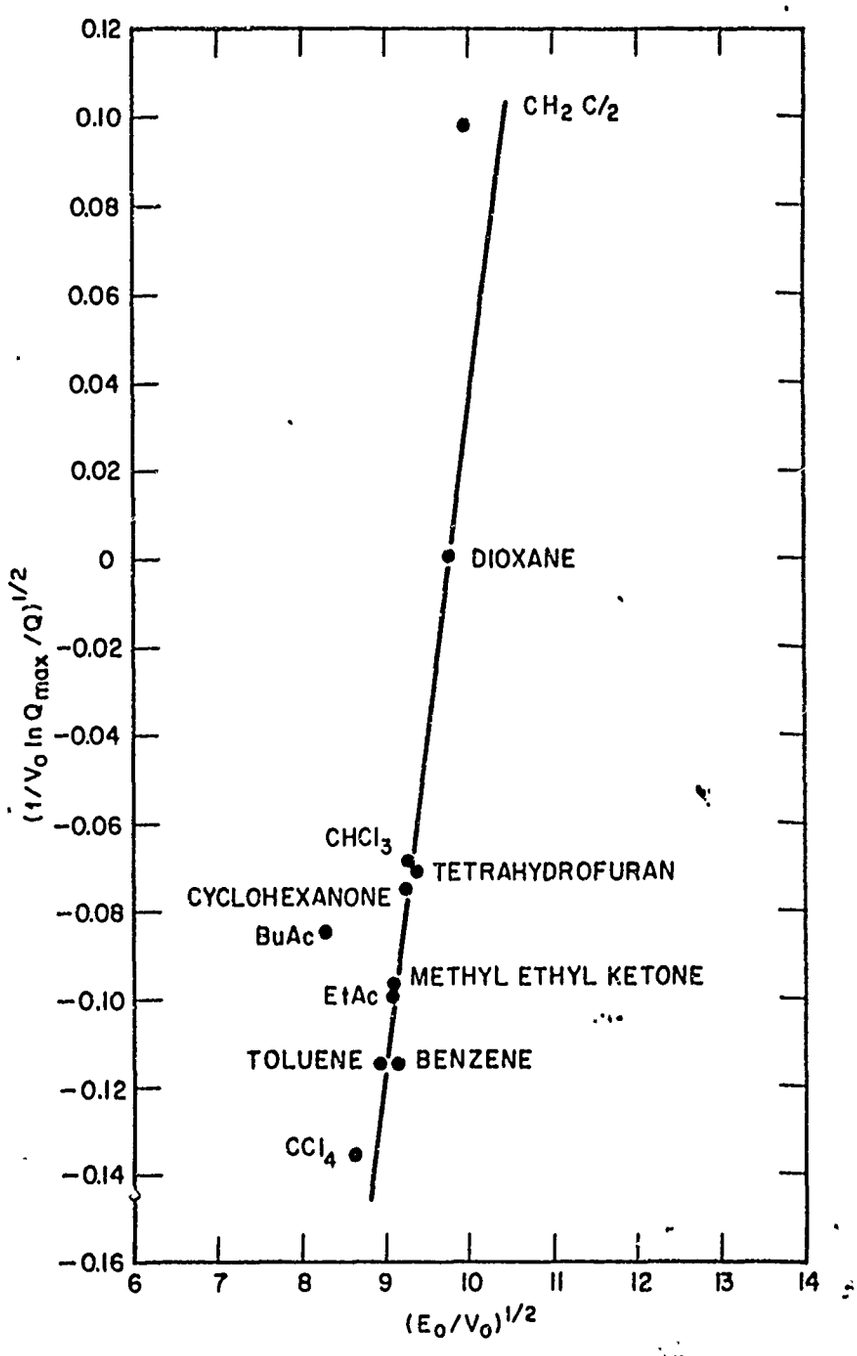

Figure 5 – Determination of Solubility Parameter for Polyurethane Binder

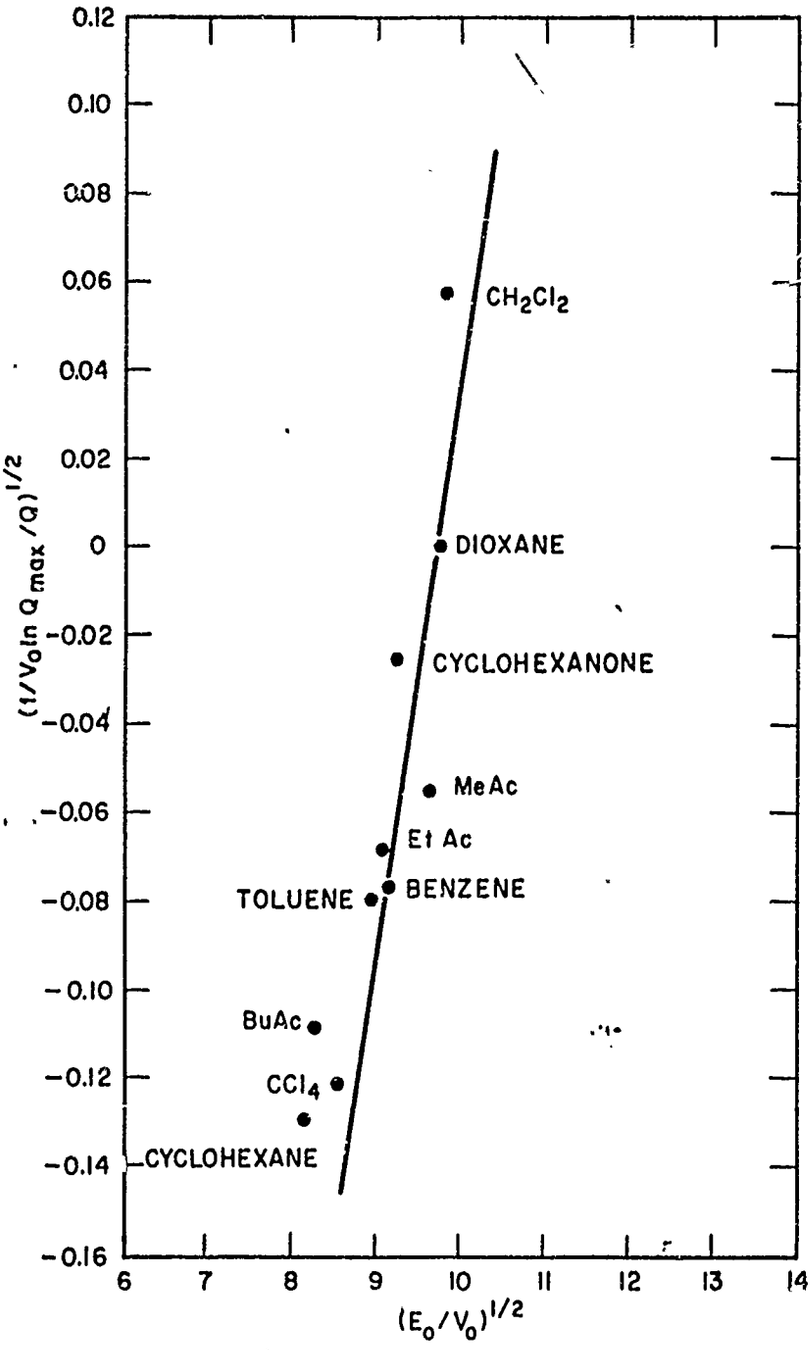

Figure 6–Determination of Solubility Parameter for Polyurethane Propellant

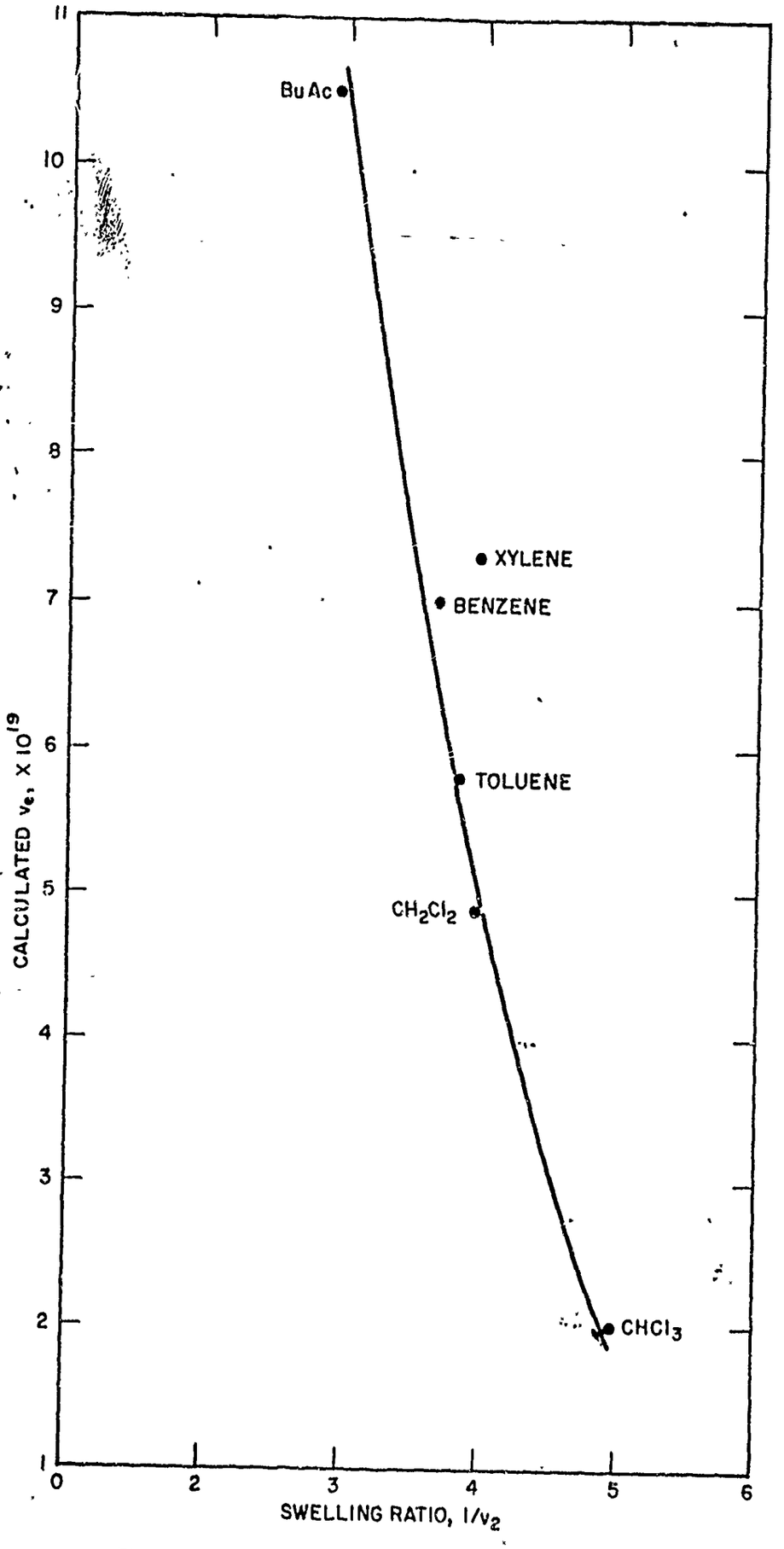

Figure 7– Apparent ν_e for Propellant in Various Solvents

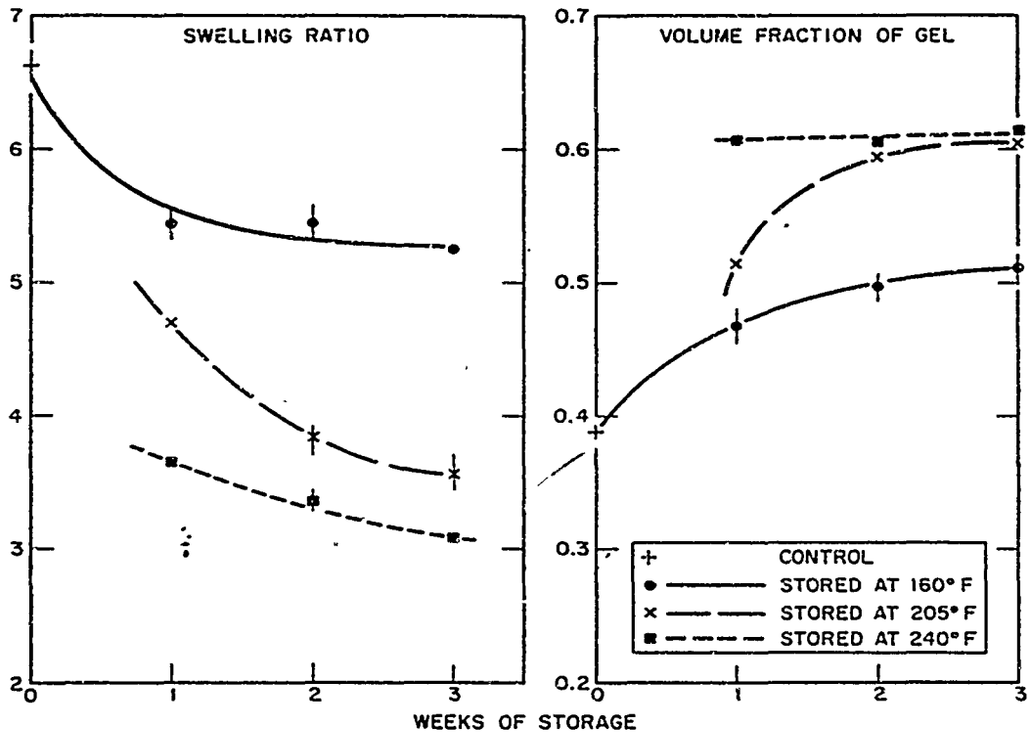

Figure 8 - Propellant No. IV

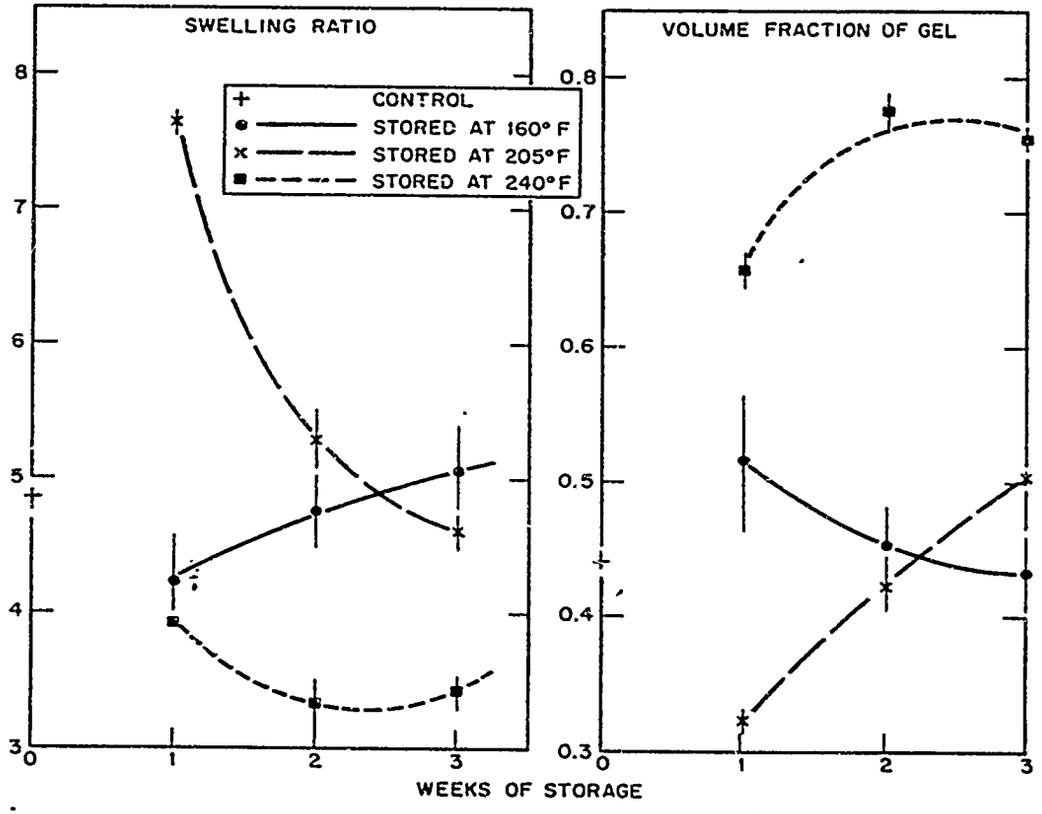

Figure 9 - Propellant No. V

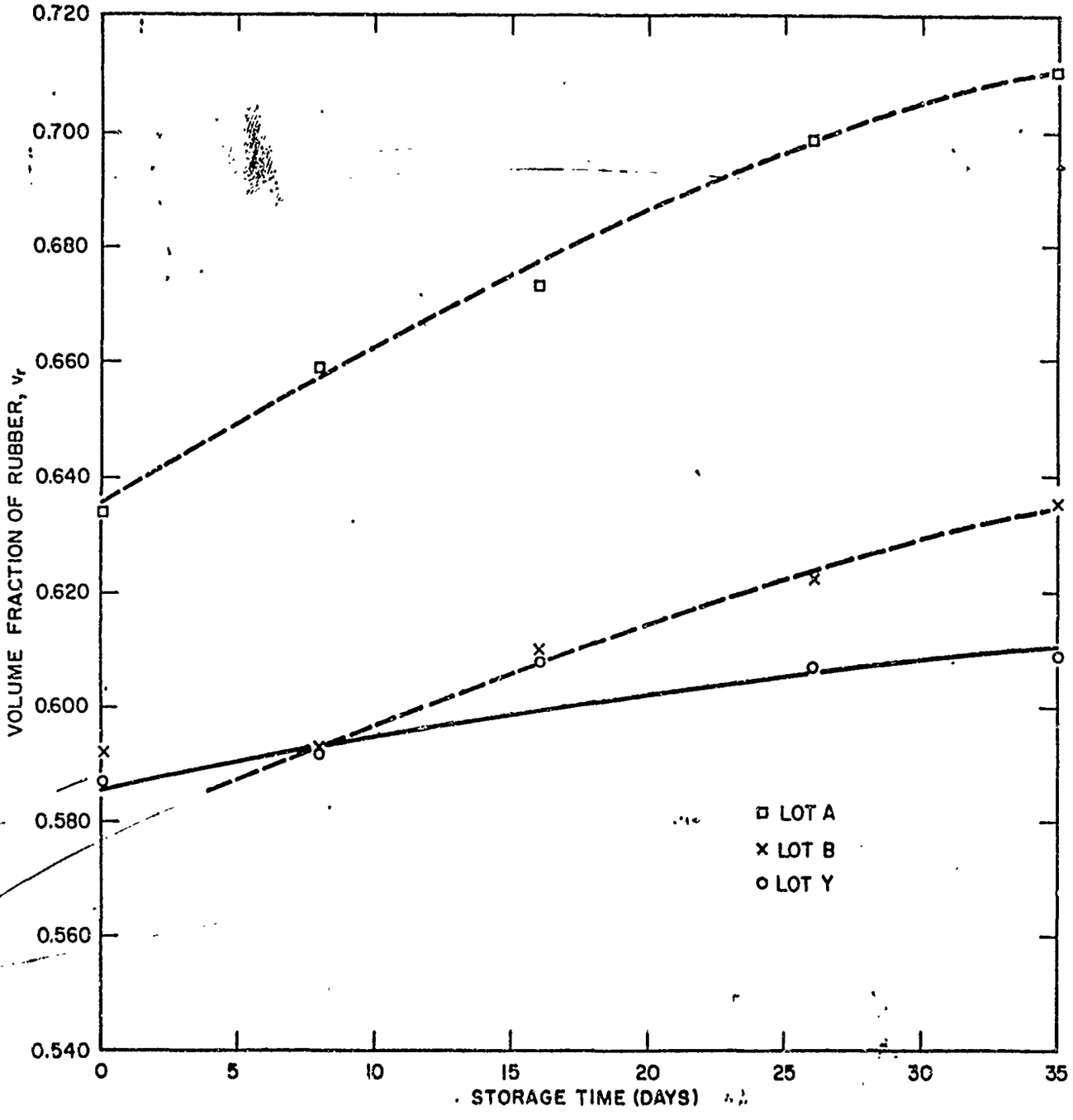

Figure 10 – Change of v_r After Storage at 170° F